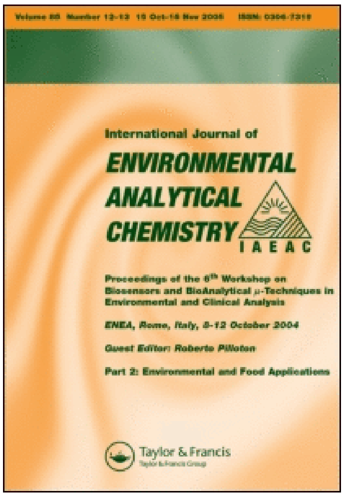

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FIELD PRECONCENTRATION OF TRACE METALS FROM SEAWATER AND BRINES COUPLED WITH LABORATORY ANALYSIS USING FLOW INJECTION AND ICP-AES DETECTION

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A simple but robust battery powered field sampling unit for the selective *in situ* preconcentration of trace elements (Cd, Co, Cu, Mn, Ni, Pb and Zn) from natural waters on a commercially available iminodiacetate resin is described. Water samples were filtered (0.45 μm) on-line and passed through twin microcolumns containing the resin Metpac CC-1. This allowed duplicate samples to be preconcentrated in parallel. The microcolumns were then taken to the laboratory and placed in a flow injection manifold coupled to an inductively coupled plasma – atomic emission spectrometer (FI - ICP-AES) for elution and quantitation. The results for CASS-2, a coastal seawater CRM, preconcentrated for 2 h at 0.5 ml min^{-1}, gave good agreement with certified values for Cd, Co, Cu, Mn, Ni and Zn. The preconcentration column has been shown to be applicable to samples in the salinity range 39 – 156 ‰ for Cd, Co, Mn and Zn and the field sampling unit is therefore suitable for the analysis of seawaters and industrial brines (such as those associated with North Sea oil field production waters).

Keywords: Flow injection; *in situ* preconcentration; ICP-AES; seawater; brines; trace metals

INTRODUCTION

The determination of trace metals in seawater can be achieved using ICP-AES (or ICP-MS) detection but matrix interferences and ultra-trace levels often require the use of solid phase chelating resins for matrix removal and analyte preconcentration[1]. This is most conveniently done with a microcolumn incorporated in a flow injection (FI) manifold and interfaced with the detector. Several

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types of resin have been used in microcolumns, with iminodiacetate and quinolin-8-ol being the most popular [2].

An additional concern with seawater is the need to maintain the integrity of the sample during storage. *In situ* preconcentration is therefore attractive because the analyte(s) are preconcentrated at source under relatively mild conditions (e.g. no acidification), the matrix is removed at source (minimising biological and chemical transformations), sample handling is minimised and the microcolumns are stable and easy to transport. Examples of microcolumns deployed in rivers include Amberlite XAD-2 for aluminium species (after complexation with quinolin-8-ol) [3], sulphydryl cotton fibre for organic mercury species [4] and gold [5] and activated alumina for inorganic chromium species [6]. *In situ* microcolumn deployment has focused on river waters because in saline matrices the dissolved salts lead to non-selective retention of matrix ions that reduces column capacity and can cause changes in the physical characteristics of the resin. This problem is even more acute when sampling high ionic strength brines such as produced waters associated with oil exploration and production.

In 1992, the volume of produced water discharged into the Norwegian sector of the North Sea was 23 million m^3, and this is forecast to increase to 90 million m^3 by the turn of the century [7]. Produced water originates mainly from the oil-bearing reservoir where it is intermixed with the oil. In the early operation of a field the water content is low but due to breakthrough of water from outside the reservoir, or water injection to improve oil recovery, produced water represents an increasing fraction of the production stream as the field ages [8]. This water contains inorganic compounds, such as heavy metals and minerals from the geological formation, in concentrations that are elevated compared with open ocean seawater [9]. Before discharge, oil is removed from the water by passing the mixture through gravity separation equipment, where demulsifiers and corrosion inhibitors are added.

The concentration of total dissolved solids in produced waters varies from field to field but in the North Sea is typically 12,750 – 24,390 mg l^{-1} Cl in northern areas and 29,927 - 165,210 mg l^{-1} Cl in southern areas [10]. As in seawater, the major cations are sodium and chloride but other metal ions may also be present, e.g. barium (up to 100 mg l^{-1}), beryllium (0.02–0.2 mg l^{-1}), cadmium (0–0.001 mg l^{-1}), copper (0.5–3 mg l^{-1}), iron (trace–1000 mg l^{-1}), lead (trace–100 mg l^{-1}), nickel (<0.001–0.015 mg l^{-1}) and zinc (trace–500 mg l^{-1}) [11].

This paper describes the design and construction of a robust, battery powered field sampling unit for the preconcentration of trace metals from seawater and brines. The unit includes in-line filtration and twin iminodiacetate (Metpac CC-1®) microcolumns. Samples have been quantitatively preconcentrated for up to 3 h at 0.5 ml min^{-1} and determined by FI – ICP-AES. The method was validated using a coastal seawater CRM (CASS-2) preconcentrated for 2 h and good agreement with certified values was obtained for Cd, Co, Cu, Mn, Ni and Zn. By continuously loading sample onto the column, breakthrough curves for Mn and Zn have been obtained in matrices of 39 – 156 ‰ salinity and breakthrough volumes predicted for 10 metal ions in 14 North Sea produced waters.

EXPERIMENTAL

Reagents

All reagents were of the highest purity obtainable from Merck BDH (Poole, Dorset, U.K.) and prepared fresh each day. All solutions were prepared with de-ionised water (18 MΩ cm) from a Milli-Q analytical reagent grade water purification system (Millipore, Bedford, MA, USA). A 2 M stock solution of ammonium acetate buffer was prepared by mixing appropriate amounts of acetic acid (Aristar) and ammonia solution (Aristar) and diluting to volume. Prior to sampling, a 0.05 M ammonium acetate solution was prepared by dilution of the stock and cleaned by passing twice through 10 cm of Chelex-100® (Na form) in a 75 ml glass column (1 cm i.d.) and stored in acid washed polypropylene containers. The chelating resin (50–100 mesh; 0.4 meq ml^{-1} determined as Cu(II)) was obtained from Sigma (Poole, Dorset, UK). The pH of the buffer was adjusted to 5.5 by addition of appropriate volumes of 2 %v/v nitric acid and the reagent pumped into collapsible medical plasma bags and sealed ready for use.

Standard solutions were prepared by dilution from 1000 mg l^{-1} Spectrosol solutions (BDH, Poole, Dorset, UK). Artificial brines were prepared by dissolving appropriate quantities of a seawater corrosion test mixture (BDH, Poole, Dorset, U.K.) in water. Standard solutions in brine were prepared by spiking with appropriate volumes of commercial stock solutions (1000 mg l^{-1} Spectrosol, BDH, Poole, UK). Nitric acid eluent (2 M) was prepared by diluting nitric acid (Aristar) with water. National Research Centre of Canada certified reference materials of open ocean seawater (NAAS-4) and coastal seawater (CASS-2) were obtained from the Bureau of Analysed Samples (Middlesbrough, Cleveland, UK) and used for method development and validation.

Field sampling

A schematic diagram of the two channel field sampling unit is shown in Figure 1. For each channel, separate buffer and sample (or standard) streams were pumped at 0.5 ml min^{-1} via a 4 channel peristaltic pump (Ismatec SA, Glattbrugg – Zurich, Switzerland) equipped with 0.51 mm i.d. Tygon® peristaltic pump tubing. A rechargeable 6 V D.C. battery or a stabilised D.C. supply provided power for the pump. PTFE tubing (0.7 mm i.d.) was used for all flow lines. After mixing with buffer at a T-piece, each sample stream was filtered in-line by passing through a 25 mm diameter, 0.45 μm pore size nylon membrane disk (Supelco, Poole, Dorset U.K). Each sample stream then passed through a Metpac CC-1 microcolumn (Dionex, UK; theoretical column capacity 0.45 meq; column volume 628 μl) containing a macroporous styrene/divinylbenzene resin covalently bonded with iminodiacetate functional groups. The complete manifold was enclosed in a polypropylene box (256 x 178 x 164 mm, RS Components, Corby, Northants, U.K.

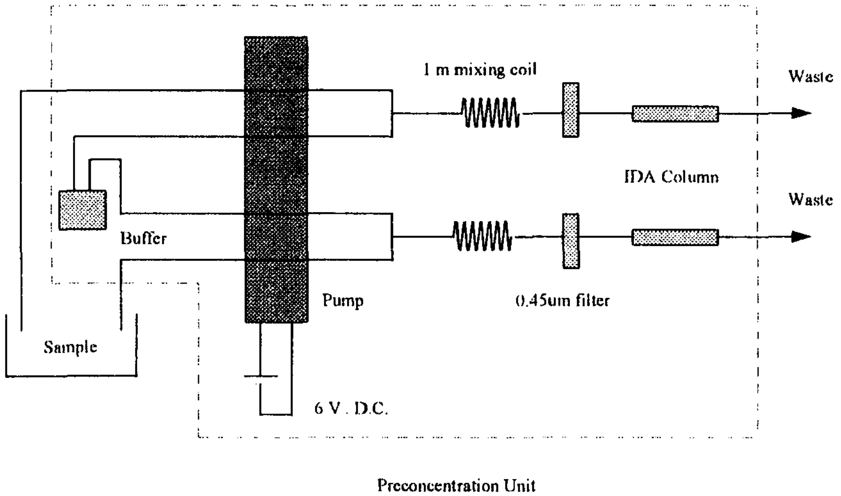

FIGURE 1 Schematic diagram of the preconcentration manifold for *in situ* field sampling

Laboratory instrumentation and procedures

An ICP-AES with a segmented array, charge coupled device detector (Optima 3000, Perkin Elmer Corp., CT, U.S.A.) was used throughout this work. Signals for all analytes were recorded simultaneously over the elution peak and areas were calculated using FigP. Optimised operating conditions are given in Table I. The single line FI manifold was constructed from PTFE tubing (0.7 mm i.d.) and incorporated a Dionex Metpac CC-1 microcolumn from the field sampling unit. Acetate buffer was pumped through the column at 1.0 ml min^{-1} for 5 min using

0.63 mm i.d. Tygon® peristaltic pump tubing, via a 4 channel peristaltic pump (Gilson, Villiers-le-Bel, France), with the eluent directed to waste via a manual switching valve. 2 M nitric acid (0.5 ml) was then injected upstream of the microcolumn via a rotary valve (Rheodyne 5401 4-way valve) and the eluent directed to the detector.

TABLE I Plasma operating conditions for ICP-AES

R.F. Power	1250 W
Nebuliser Flow (Ar)	0.9 l min^{-1}
Auxiliary Flow (Ar)	1 l min^{-1}
Plasma Flow (Ar)	15 l min^{-1}
Viewing height	12 mm

To obtain breakthrough curves, appropriate quantities of artificial seawater mix (34.5 g and 138.9 g) were dissolved in water to give brines of 35 and 140 ‰ salinity respectively. These brines were spiked with 1000 mg l^{-1} Spectrosol standard solutions of Mn and Zn, to give 10 mg l^{-1} of each analyte in each brine sample, and used to predict breakthrough volumes for intermediate salinity brines. A 71 ‰ brine containing 10 mg l^{-1} of a mixed standard (Cd, Co, Mn and Zn) was used to test these predictions. Each sample was pumped continuously at 0.5 ml min^{-1} and merged with buffer (also pumped at 0.5 ml min^{-1}) before passing through the column. The eluent was monitored continuously for 15 min and then at 5 min intervals using the ICP-AES detector. Breakthrough data were obtained by plotting the volume of solution passed through the column versus the concentration of the breakthrough ion as it appeared in the eluent. Once breakthrough for all analytes of interest was complete, acidic eluent was introduced into the sample stream to elute the retained species. The column was then conditioned for 10 min with buffer before the next experiment was carried out.

RESULTS AND DISCUSSION

Sample preconcentration

The objective of the field sampling unit was to allow remote preconcentration of target analytes from saline waters over extended periods of time. The unit was therefore used to preconcentrate NASS-4 spiked with a 10 μg l^{-1} multielement standard, containing Cd, Co, Cu, Mn, Pb and Zn, for periods of 5, 15, 30, 60, 90 and 120 min at a flow rate of 0.5 ml min^{-1}. Blanks (Milli-Q water) were also preconcentrated for the same periods of time. The microcolumns were then eluted with 0.5 ml of 2 M nitric acid using the laboratory FI manifold with ICP detection [12]. The resultant calibration plots (blank subtracted) for peak area versus concentration were linear for Co, Cu, Mn and Zn (0.985 > r < 0.990) but had slight curvature at low concentrations for Cd and Pb.

Additional experiments were performed in the laboratory to simulate longer preconcentration times by directly loading 1 ml of NASS-4 certified reference material, spiked with a multielement standard at concentrations of up to 10 mg l^{-1}, on the microcolumn (equivalent to preconcentrating the 10 μg l^{-1} standard at 0.5 ml min^{-1} for 32 h). Calibration plots for the eluted peaks were linear for all elements (0.986 > r <0.999). Parallel experiments in Milli-Q water gave calibration plots with very similar gradients to the seawater matrix, suggesting that aqueous standards could be used to calibrate for seawater samples.

In order to determine the minimum sample volumes required for detection when deploying the field sampling unit in different environmental situations, multielement standards for the seven elements listed in Table II, covering the range 1 – 500 μg l^{-1}, were prepared in Milli-Q water. These were analysed using the laboratory FI manifold with a 1 ml sample loop and the detection limits, based on blank + 3 s (n = 10), are given in Table II in concentration and absolute units. The field unit is operated at 0.5 ml min^{-1} so the detection limit values are equivalent to a 2 min preconcentration time.

The reproducibility of the pump in the field sampling unit was evaluated for each of the four channels over various periods of time up to 300 min and was found to be < 5.0 % rsd (n=5) for all experiments. The 6 V battery used with the unit began to lose power after 5 h of continuous use. The repeatability (n = 3, analysed on three separate days) of the complete process (field sampling and laboratory analysis) for a 10 μg l^{-1} multielement seawater standard (spiked NASS-4) was < 10 % for all six elements for preconcentration times of 5 – 120 min.

Recoveries with CASS-2

The protocol for the determination of selected elements in CASS-2 (Cu, Mn, Ni, Zn) was as follows. Aqueous multi-element standards at 0.001, 0.01, 0.1 and 0.5 μg l^{-1} were prepared in acid washed PPE graduated flasks by serial dilution from 1000 mg l^{-1} Spectrosol stock solutions. Calibration data were obtained by loading 1.0 ml of each standard in duplicate (i.e. on both columns) before eluting with 0.5 ml of acid. Each standard was analysed in triplicate. Duplicate CASS-2 samples were preconcentrated on the two microcolumns in the field sampling unit for 3 h. Blanks were also obtained by preconcentrating Milli-Q water for 3 h. After each preconcentration, the microcolumns were rinsed for 15 min with ammonium acetate buffer to remove any matrix ions and then placed in the FI manifold and analysed as described above. Peak areas were calculated, blank subtracted, and quantified using the aqueous calibration data. The results, obtained in absolute units and converted back to $\mu g\ l^{-1}$ in the original sample, are shown in Table III. There was good agreement with certified values for all four elements.

TABLE II Analytical wavelengths for the seven elements investigated and limits of detection (mean blank + 3 s) for a Milli-Q water matrix with a 1.0 ml sample loop and analysis by FI – ICP-AES

Element	*Wavelength nm*	*Limit of Detection (for 1 ml loop)*	
		$\mu g\ l^{-1}$	μg
Cd	228.802	1.5	0.0015
Co	228.616	6.8	0.0068
Cu	324.754	0.5	0.0005
Mn	257.610	0.4	0.0004
Ni	341.476	7.6	0.0076
Pb	283.306	38	0.038
Zn	213.856	0.7	0.0007

TABLE III Validation data for *in situ* preconcentration using CASS-2. Sample was loaded for 120 min at 0.5 ml min^{-1}

Analyte	*Experimental ± 2s* $\mu g\ l^{-1}$	*Certified ± 2s* $\mu g\ l^{-1}$
Cu	0.715 ± 0.047	0.675 ± 0.039
Mn	2.11 ± 0.19	1.99 ± 0.15
Ni	0.270 ± 0.066	0.298 ± 0.036
Zn	1.95 ± 0.15	1.97 ± 0.12

The field sampling unit was also used in Plymouth Sound, South West England on board the research vessel RV Tamaris using the preconcentration procedure described above. Seawater (salinity 33 ‰) was collected in bulk, acidified with nitric acid (to give 1 %v/v) and then pumped through the unit for 3 h. The results (µg l^{-1} ± 2s) for triplicate analyses, each run in duplicate, were 0.019 ± 0.005 for Cd, 0.007 ± 0.006 for Co, 0.769 ± 0.070 for Cu, 1.08 ± 0.08 for Mn, 0.129 ± 0.030 for Ni and 2.66 ± 0.113 for Zn. These data are in good agreement with published results for the same location, salinity and season [13] and demonstrate the effectiveness of this approach.

Breakthrough curves in brines

The field unit is suitable for deployment in marine environments such as coastal waters but in order to be able to use it for monitoring production waters, the capacity of the microcolumns in high ionic strength brines was investigated. 140 ‰ brine was spiked with 10 mg l^{-1} of Mn and Zn and the solution pumped continuously through the microcolumn at 0.5 ml min^{-1}. Breakthrough curves for Mn and Zn in the brine are compared with those in seawater in Figures 2 and 3 respectively. The breakthrough volume was defined as the volume of sample eluted when the analyte signal at the detector reached 10 % of the maximum steady state signal. Breakthrough volumes were 2.5 ml and 112.5 ml for Mn and Zn respectively in seawater and 0.4 ml and 15 ml respectively in 140 ‰ brine.

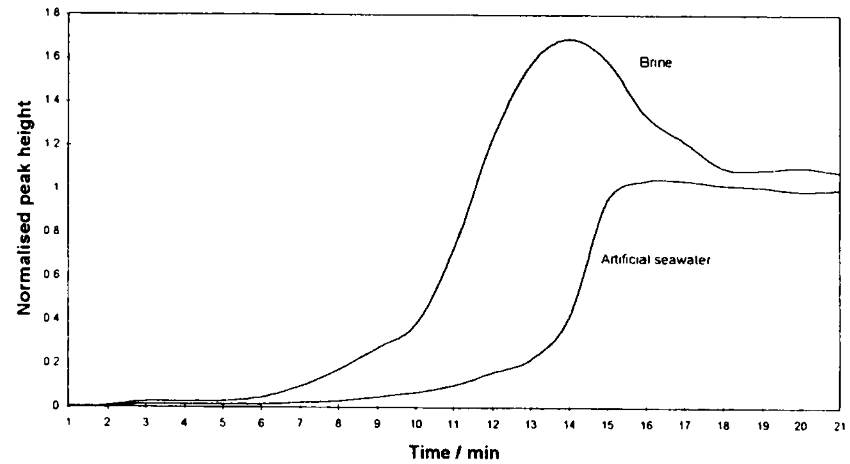

FIGURE 2 Normalised breakthrough curves for Mn in artificial seawater (salinity 35‰) and brine (salinity 140‰) with 0.05 M ammonium acetate buffer

The breakthrough volume for any ion should be directly related to its concentration and the selectivity factor of the Metpac microcolumn for that ion. Further-

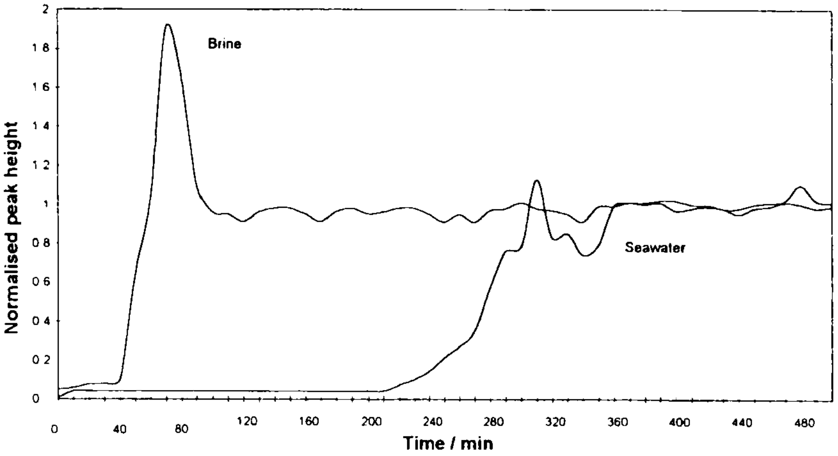

FIGURE 3 Normalised breakthrough curves for Zn in artificial seawater (salinity 35 ‰) and brine (salinity 140 ‰) with 0.05 M ammonium acetate buffer

more one would expect the breakthrough volume to be inversely proportional to the strength of the brine. Predicted breakthrough volumes, based on the experimental data for Zn, for fourteen ions at 10 mg l^{-1} are given in Table IV for 35 and 140 ‰ brines. There is good agreement between the predicted and experimental breakthrough volumes for Mn; 2.7 and 2.5 ml in 35 ‰ brine and 0.4 and 0.4 ml in 140 ‰ brine respectively. In order to further test the validity of the predictions a 71 ‰ brine (equivalent to Forties field formation water) was spiked with Zn, Co, Cd and Mn at 10 mg l^{-1} and the four experimental breakthrough curves determined simultaneously (Figure 4). The predicted breakthrough volumes and calculated resin selectivities correlated well with experimental and published [14] values (-20 % bias). These results are presented in Table V. Using the same approach, breakthrough volumes for 10 metal ions in formation waters of varying salinity from 14 North Sea oil and gas fields have been predicted and are shown in Table VI.

Effect of buffer concentration on breakthrough curves

Using a buffer of 0.05 M ammonium acetate at pH 5.5, the breakthrough curves exhibited a peak as breakthrough occurred (Figures 2–4), before returning to a steady state signal that corresponded to the response for a continuously aspirated sample.

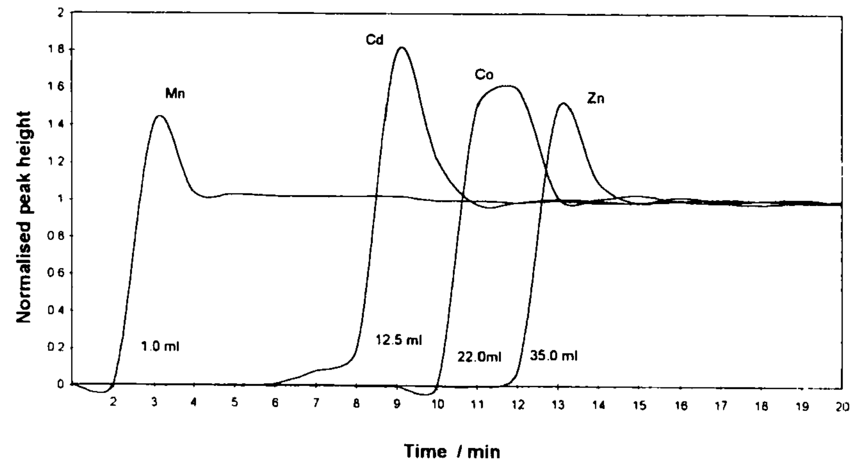

FIGURE 4 Normalised breakthrough curves for Mn, Zn, Co, Cd at 10 mg l^{-1} in 71 ‰ brine (equivalent to a Forties field formation water) with 0.05 M ammonium acetate buffer

TABLE IV Predicted breakthrough volumes for 10 mg l^{-1} standards in 35 ‰ seawater and 140 ‰ brine. Selectivity factors normalised to 1.00 for zinc

Analyte	*Selectivity factor for IDA resin [14]*	*Breakthrough volume in 35 ‰ seawater (ml)*	*Breakthrough volume in 140 ‰ brine (ml)*
Na	10^{-7}	<0.1	<0.1
Mg	0.009	<0.1	<0.1
Sr	0.013	<0.1	<0.1
Ca	0.013	<0.1	<0.1
Ba	0.016	1.8	0.25
Mn	0.024	2.7	0.40
Fe	0.130	15	2.0
Cd	0.390	44	5.9
Co	0.615	69	9.3
Zn	1.00	110	15
Pb	3.88	440	58
Ni	4.40	500	66
Cu	126	14,000	1900
Hg	1060	120,000	16,000

TABLE V Predicted and experimental breakthrough volumes and selectivities for analytes present at 10 mg l^{-1} in a 71 ‰ salinity brine

Analyte	*Predicted breakthrough volume (ml)*	*Experimental breakthrough volume (ml)*	*Selectivity of IDA for analyte*	*Experimentally derived selectivity*
Cd	12	13	0.390	0.391
Co	19	22	0.615	0.619
Mn	0.70	1.0	0.024	0.023
Zn	30	34	1.000	0.890

TABLE VI Predicted analyte breakthrough volumes (ml) in North Sea formation waters of high salinity when present at 10 mg l^{-1} and preconcentrated on Metpac CC-1 resin with 0.05 M ammonium acetate buffer

Field	*Brine to seawater salinity ratio*	*Ba*	*Mn*	*Fe*	*Cd*	*Co*	*Pb*	*Ni*	*Cu*	*Hg*	*Zn*
Amethyst	6.7	0.14	0.20	1.1	3.3	5.2	33	37	1100	9000	8.5
Esmond	1.4	0.65	0.97	5.3	16	25	160	180	5100	43000	40
Hyde	6.8	0.13	0.20	1.1	3.3	5.1	32	37	1100	8800	8.3
Westphalia	7.7	0.12	0.18	1.0	2.9	4.5	29	32	930	7800	7.4
Beatrice	1.5	0.59	0.88	4.8	14	22	140	160	4600	39000	37
Forties	2.3	0.40	0.60	3.3	9.8	15	97	110	3200	27000	37
Miller	2.0	0.45	0.70	3.7	11	17	110	120	3600	60000	25
Thelma	3.0	0.30	0.45	2.4	7.2	11	71	81	2300	20000	28
Brent South	0.60	3.3	5.0	26	80	130	800	910	26000	220000	19
Magnus	0.77	3.0	4.5	24	72	110	720	820	23000	200000	210
Snore	1.1	0.82	1.2	13	40	63	400	450	13000	110000	100
Troll	1.1	0.80	2.7	13	39	61	390	440	13000	110000	100
Heldrun	2.5	0.36	0.55	2.9	8.7	13	86	98	2800	24000	22
Tyrlhaus	1.6	0.54	0.90	4.5	13	42	130	150	4300	36000	69

This profile was particularly noticeable when analysing the concentrated brines. The experiments in 71 ‰ brine spiked with 10 mg l^{-1} Mn and Zn were therefore repeated with 0.2 M ammonium acetate buffer, and the breakthrough curves are shown in Figures 5 and 6, respectively.

The absence of a peak with the stronger buffer can be explained by its higher buffering capacity. The Metpac resin is a weak acid / weak base and as metal ions are retained, H^+ ions are displaced into the carrier stream. In the presence of a high concentration of matrix ions, the large number of H^+ ions liberated reduces the on-column pH, giving rise to temporarily reduced preconcentration efficiency and column capacity. Use of higher concentration ammonium acetate buffers these liberated H^+ ions, which restores column equilibrium, increases the column capacity and reduces the size of the peaks. However, because it is unlikely that breakthrough volumes will be reached with real samples, the lower concentration buffer is recommended in order to minimise blank signals.

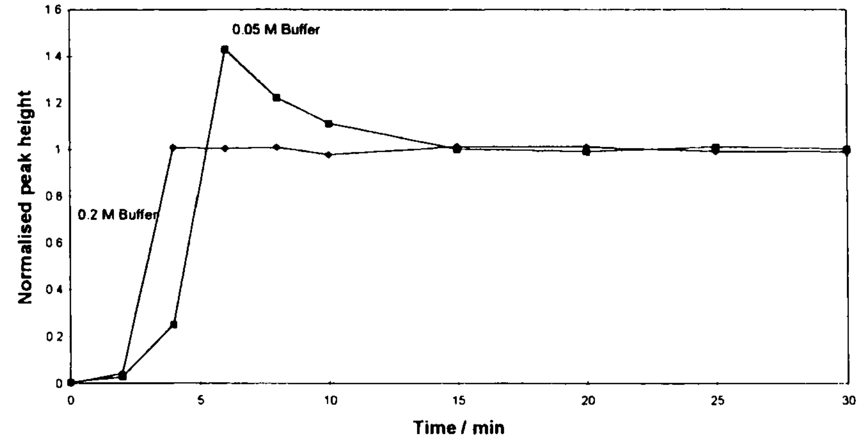

FIGURE 5 Normalised breakthrough curves for Mn in 140 ‰ brine with 0.05 M and 0.2 M ammonium acetate buffer at pH 5.6

CONCLUSIONS

A robust and portable field sampling unit incorporating two iminodiacetate resin microcolumns has been shown to be suitable for *in situ* preconcentration of trace metals (Cd, Co, Cu, Mn, Ni, Pb and Zn) from seawater and industrial brines. The microcolumns can easily be incorporated in an FI manifold with ICP-AES detection and the response was linear for up to 5 h of preconcentration. Breakthrough volumes for the microcolumn correlate well with literature selectivity factors for 14 elements and breakthrough volumes for 10 elements in North Sea formation waters from 14 fields have been predicted.

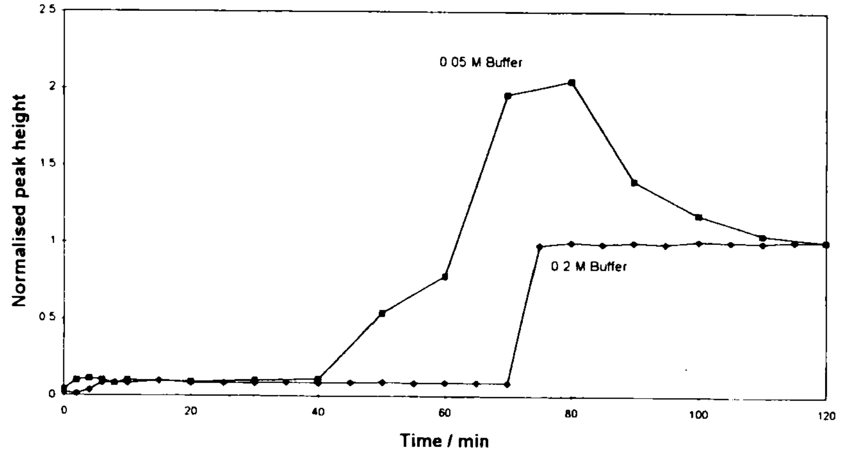

FIGURE 6 Normalised breakthrough curves for Zn in 140 ‰ brine with 0.05 M and 0.2 M ammonium acetate buffer at pH 5.6

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